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OFFICE OF NAVAL RESEARCH  
FINAL TECHNICAL REPORT

Grant N00014-89-J-1767

**A Novel Approach to Silicon-on-Insulator Materials**

Alan H. Cowley

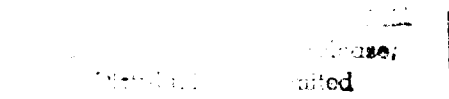
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**92-06846**



## FINAL TECHNICAL REPORT

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## a. Papers Submitted to Refereed Journals (and not yet published)

None

## b. Papers Published in Refereed Journals

- M. J. Benac, A. H. Cowley, R. A. Jones and A. F. Tasch, "Growth of Polycrystalline  $\text{CaF}_2$  via Low Temperature Organometallic Chemical Vapor Deposition", *Chemistry of Materials*, **1**, 289, (1989).
- A. H. Cowley, "Development of Single Source Precursors for the Production of Electronic Materials," *Anal. of the First Symposium on Materials Science: Santiago, Chile, 1989*, **1**, 65.
- R. A. Jones, "Synthesis of Novel Organometallic Precursors for Electronic Materials," *Anal. of the First Symposium on Materials Science: Santiago, Chile, 1989*, **1**, 89.
- A. H. Cowley, "From Multiple Bonds to Materials Chemistry, *J. Organomet. Chem.*, **400**, 71 (1990).

## c. Books (and sections thereof) Submitted for Publication

- A. H. Cowley, "Organometallic Chemical Vapor Deposition of GaAs and Related Semiconductors Using Novel Organometallic Precursors", *IUCCP Symposium Volume on Metal-Metal Bonds and Clusters in Chemistry and Catalysis*, Plenum Publishers, p. 195 (1990).

## d. Books (and sections thereof) Published

None

## e. Patents Filed

Statement A per telecon  
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None

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## f. Patents Granted

- A. H. Cowley, R. A. Jones, and A. F. Tasch, "Growth of Polycrystalline  $\text{CaF}_2$  Via Low Temperature OMCVD", U.S. Patent # 5,026,575, June 25, 1991.

Approved For

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**g. Invited Presentations at Topical or Scientific/Technical Society Conferences**

A. H. Cowley presented the lecture entitled, "Novel Organometallic Routes to Electronic Materials" at the following locations:

- Pontificia Universidad Catolica de Chile, Santiago, Chile - November 30, 1989
- Pettit Memorial Symposium, Southwest Regional ACS Meeting, Baton Rouge, Louisiana - December 7, 1989.
- Pacificchem Conference, Honolulu, Hawaii - December 19, 1989.
- University of Kentucky, Lexington, Kentucky - February 27, 1990.
- University of Texas at Arlington - March 2, 1990.
- Brandeis University, Waltham, Massachusetts - April 9, 1990.
- International Symposium on Phosphorus Chemistry, Lodz, Poland - June 25, 1990.
- Canadian Institute of Chemistry Congress, Halifax, Nova Scotia, Canada - July 19, 1990.
- International Conference on Organometallic Chemistry, Detroit, Michigan - August 23, 1990.
- Symposium on Inorganometallic Chemistry, National American Chemical Society Meeting, Washington, D. C. - August 30, 1990.
- University of New Brunswick, Fredericton, New Brunswick, Canada - September 24, 1990.
- Université de Moncton, Moncton, New Brunswick - September 24, 1990.
- University of Prince Edward Island, Charlottetown, Prince Edward Island - September 26, 1990.
- Memorial University, St. Johns, Newfoundland - September 27, 1990.
- Dalhousie University, Halifax, Nova Scotia - September 28, 1990.
- University of Rochester, Rochester, New York - October 25, 1990.
- Weissberger Lecturer, Eastman Kodak, Rochester, New York - October 26, 1990.
- Presentation of paper at the Southwest Regional Meeting of the National American Chemical Society, New Orleans, Louisiana - December 6, 1990.
- Invited lecture presented at Fourth Meeting of Inorganic Chemists, Valparaiso, Chile - January 9, 1991.
- University of Kansas, Lawrence, Kansas - January 24, 1991.
- Dielectrics and CVD Metallization Symposium, La Jolla, California - February 12, 1991.

- Seminar speaker at PPG Industries, Pittsburgh, Pennsylvania - March 14, 1991.
- Invited colloquium at Texas A&M, College Station, Texas - March 20, 1991.
- Invited lecture presented at the Concoord Conference, Bombannes, France - May 14, 1991.
- Invited seminar presented at Université de Bordeaux, Bordeaux, France - May 20, 1991.

R. A. Jones presented the lecture entitled, "The Synthesis of New Organometallic Compounds as Precursors to Electronic Materials" at the following locations:

- Dow/Sikorski - Hartford, Connecticut - January 31, 1990.
- Florida Advanced Materials Conference, Palm Coast, Florida - June 4, 1990.
- Exxon Chemical Company, Baytown, Texas - July 13, 1990.
- Invited Lecture, Chemical Society Meeting, Glasgow, Scotland, UK - October 19, 1990
- Invited Lecture, Kodak Tennessee Eastman, Tennessee - October 26, 1990.
- Invited Lecture, Materials Research Society Meeting, Boston, MA - November 26, 1990
- Presentation of Paper, New Orleans ACS Meeting, Louisiana - December 6, 1990.
- Invited Lecture, Silicon Symposium, El Paso, Texas - April 12, 1991.
- Invited Lecture, Olin Corporation, Hartford, Connecticut - April 26, 1991.
- Invited Lecture, Lazer Save Corporation, Toronto, Canada - April 27, 1991.

**h. Contributed Presentations at Topical or Scientific/Technical Society Conferences**

- A. H. Cowley, "Novel Organometallic Routes to Electronic Materials", Seventh Annual IUCCP Symposium, Texas A&M University, March 20, 1989.

**i. Honors / Awards / Prizes**

None

**j. Graduate Students and Postdoctorals Supported Under the CRP for the Year Ending 31 May 1991**

- John W. Nail

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**The University of Texas at Austin**

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### **Final Technical Report**

#### *Introduction and Background*

There is currently a great deal of interest in insulator on semiconductor layer constructions in the electronics community. Calcium fluoride is electronically insulating and lattice matched to both silicon and gallium arsenide, which makes it an ideal insulator for these materials. Also,  $\text{CaF}_2$  is being used as an insulator with thin films of the high temperature superconducting materials. While there has been a great deal of work in the deposition of  $\text{CaF}_2$  films by physical techniques, such as molecular beam epitaxy (MBE), this technique is not considered to be viable for large scale production techniques due to the expensive and sophisticated high vacuum equipment involved. Another problem with MBE of  $\text{CaF}_2$  is that high substrate temperatures ( $\geq 500^\circ\text{C}$ ) seem to be required for good quality films. Due to the differences in thermal expansion between  $\text{CaF}_2$  and silicon or gallium arsenide, these films tend to crack when cooled to ambient temperature. Therefore, a project was undertaken to see if  $\text{CaF}_2$  films could be grown by chemical methods. The most useful of these is the Chemical Vapor Deposition (CVD) method, where the material of interest is produced by a chemical reaction on the substrate surface by one or more precursor molecule(s), which are delivered to the substrate in the gas phase.

For a binary material, such as  $\text{CaF}_2$ , there are two CVD growth methods. In a dual source method, two precursors are used, each of which contains one of the elements in the film material. In the single source technique, a precursor molecule which contains both elements that comprise the film material is used. This report will describe work in which each approach was tried.

The first report of CVD film growth of  $\text{CaF}_2$  appeared in 1989.<sup>1</sup> Two single source precursors were tried, bis-(1,1,1-trifluoro-2,4-pentanedione) calcium,  $(\text{CaTFAC}_2)$ ,

and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) calcium, ( $\text{CaHFAC}_2$ ) with similar results being obtained from each precursor. Films of  $\text{CaF}_2$  were grown on silicon at a temperature of  $500^\circ\text{C}$ . These authors reported that unless the deposition reactions of these precursors are performed under oxygen-rich conditions, a large amount (approx. 50%) carbon incorporation into the film occurs.

A few months later, a second report of CVD  $\text{CaF}_2$  film grown appeared.<sup>2</sup> The precursor used was  $\text{CaHFAC}_2$ , the substrate was gallium arsenide, and the reactor pressure was  $10^{-1}$  Torr. Two experiments were performed, in one, a substrate temperature of  $350^\circ\text{C}$  was used; in the other experiment, the substrate temperature was  $100^\circ\text{C}$ , and a xenon arc lamp was used to illuminate the top of the substrate. Similar results were reported from each experiment: a fluoride deficient film of  $\text{CaF}_2$ , with a Ca : F ratio of 1 : 1.6, and less than 10% carbon and oxygen incorporation in the film. Interestingly, these authors were unable to grow  $\text{CaF}_2$  films from  $\text{CaHFAC}_2$  that was purchased from Strem Chemical Company.

It is interesting that rather different results have been obtained from the same precursor,  $\text{CaHFAC}_2$ . One group reported that oxygen was required to prevent a massive (50%) amount of carbon incorporation. The other group claims that under anaerobic conditions, the carbon and oxygen incorporation was less than 10%. The only significant experimental details were the substrates used (silicon vs. gallium arsenide) and the substrate temperatures ( $500^\circ\text{C}$  vs.  $350^\circ\text{C}$ ). It is also surprising that identical results were obtained by a  $350^\circ\text{C}$  substrate and for a  $100^\circ\text{C}$  substrate which was illuminated by a xenon lamp.

Another report of  $\text{CaF}_2$  CVD used bis-(1,1,1,2,2-pentafluoro-6,6-dimethyl-3,5-heptanedione) calcium ( $\text{Ca PPM}_2$ ) as the precursor.<sup>3</sup> Films were grown on a variety of substrates, including  $\text{MgO}$ , Si, and GaAs at a pressure of 1.5 Torr., and a substrate temperature of  $400^\circ\text{C}$ . Microwave excited (2.45 GHz, at 90 watts power) argon and oxygen were used to aid the film growth. The films contained a Ca / F ratio of 0.4 to 0.5 and "a little carbon and oxygen contamination". Oriented films were obtained, with the orientation determined by that of the substrate.

In the above reports, it appears that the oxide surfaces on the silicon or gallium arsenide substrates were not removed prior to the deposition experiments. Removal of this oxide layer from silicon leaves a very reactive surface that is prone towards oxidation, especially in oxygen rich or activated oxygen conditions. Therefore, the above reports of oxygen incorporation should be viewed with caution. If the deposition had been performed on a deoxygenated silicon or gallium arsenide surface under these conditions, presumably, the oxygen would have re-oxidized the surface, leading to higher oxygen incorporation as

Si-O, or Ga-O, As-O species. Also, the fate of the carbonyl oxygen atoms in these diketonate ligands has not been determined. Presumably, these carbonyl groups might be another source of oxygen and possibly carbon incorporation.

### *Results and Discussion*

Initial experiments in this laboratory used the dual source approach with bis-(pentamethylcyclopentadienyl) calcium ( $\text{Cp}^*_2\text{Ca}$ ) and a variety of fluorinating reagents, including silicon tetrafluoride, nitrogen trifluoride, and bis-(trifluoromethyl)peroxide as the precursor molecules.<sup>4</sup>  $\text{Cp}^*_2\text{Ca}$  was chosen as the calcium source due to its volatility and its lack of heteroatoms, such as oxygen or nitrogen. A low pressure ( $10^{-1}$  Torr) CVD apparatus, featuring a 6" diameter glass tube and a heated graphite substrate stage was constructed.

Calcium Fluoride films were grown on silicon, at a system pressure of 1 Torr. The  $\text{Cp}^*_2\text{Ca}$  sublimator temperature was  $175^\circ\text{C}$ , and helium, at a flow rate of 4mL/min. was used to help vaporize the calcium precursor. Silicon tetrafluoride was used as the fluorine source. Unfortunately, the substrate had to be kept at ambient temperature in these experiments.

While the initial results from these experiments were encouraging, some serious problems with this approach were encountered. Film growth was achieved only by heating the walls of the reactor and removing the graphite stage. It appears that the  $\text{Cp}^*_2\text{Ca}$  molecule reacts with the fluorine sources at ambient temperature, leading to deposition on cold spots in the reactor. Deposition on the substrate was only achieved by making it the coldest part of the deposition system. This constrains films growth to be performed at ambient temperature, leading to poor quality films due to the immobility of the Ca and F atoms on the growing surface at  $25^\circ\text{C}$ . Other work seems to show that good quality films are obtained only at high ( $>400^\circ\text{C}$ ) substrate temperature. Nomarski microscopy showed these films to be very rough and uneven. Analysis by XPS established that the films did consist of  $\text{CaF}_2$  with some carbon incorporation.

A more serious problem, is that HF was being produced as a by-product of the deposition reaction. After several deposition experiments were performed, corrosion of the internal metal surfaces in the reactor, such as the glass-metal transitions, was observed. Mass spectral analysis of the gaseous by-products from the reaction showed that the methyl groups on the pentamethylcyclopentadienyl ligand were undergoing fluorination.

Due to the above problems, this method was abandoned, and a search for new precursors was undertaken. The requirements for a good  $\text{CaF}_2$  precursor, then seems to be:

- 1) Sufficient volatility for vapor transport to the substrate surface at a reasonable rate,
- 2) Enough reactivity to decompose to form  $\text{CaF}_2$ , yet enough stability so that high temperature or light is required for the decomposition, so that the reaction can be controlled and deposition away from the substrate can be prevented,
- 3) The precursor should not contain active hydrogens, such as benzylic or allylic hydrogen, so that HF formation during the reaction can be avoided, and
- 4) The precursor should not contain elements such as oxygen or nitrogen bonded in the molecule in a form that is likely to lead to their becoming bonded to the substrate surface or incorporated into the  $\text{CaF}_2$  film.

These four characteristics place severe restrictions on the choices for precursor molecules. Currently, to the best of our knowledge, there are no known calcium containing molecules that are not hampered by one or more of the above problems.

#### *The Search for New Precursors*

Virtually all of the stable organo-calcium molecules are based either on cyclopentadienyl or  $\beta$ -diketonate ligands. Bis-cyclopentadienyl calcium ( $\text{Cp}_2\text{Ca}$ ) is known to be polymeric in the solid phase,<sup>5</sup> and thus has a very low vapor pressure. Nonetheless, experiments were tried with this compound; it could not be vaporized in this laboratory ( $10^{-3}$  Torr,  $200^\circ\text{C}$ ). A variety of ring-substituted cyclopentadienyl calcium molecules have been made, and have been found to be monomeric, with reasonable vapor pressures. These all, however, are very air sensitive. One would expect that if the calcium precursor is very air-sensitive, it will also be very reactive towards fluorine reagents, which would give a problem controlling the deposition reaction, leading to deposition away from the substrate.

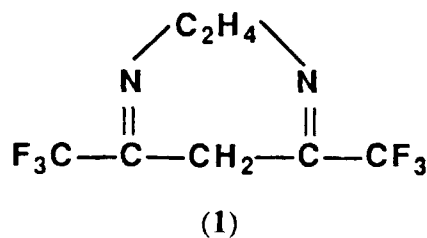
It has been shown<sup>6</sup> that the reactivities of these molecules can be moderated by using very bulky cyclopentadienyl ligands on the calcium. Thus, an attempt was made to make bis-(pentaphenylcyclopentadienyl) calcium, which should almost totally enclose the calcium ion, moderating its reactivity. The reaction between potassium pentaphenylcyclopentadienyl and calcium iodide, and the reaction between very finely divided calcium metal and pentaphenylcyclopentadiene were both tried. Unfortunately, this work was unsuccessful. It appears that this ligand may be too bulky to allow two of them to fit around a  $\text{Ca}^{+2}$  ion. While characterization has not been completed, initial results



indicate that similar reactions with tetraphenylcyclopentadiene have produced the bis(tetraphenylcyclopentadienyl) calcium molecule, although its characterization is still in progress. After it has been fully characterized, this molecule will be evaluated as a calcium source for  $\text{CaF}_2$  deposition.

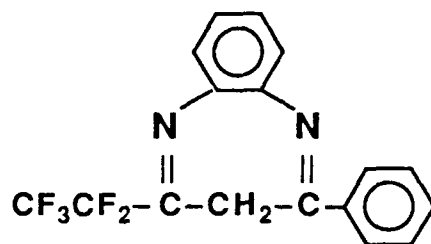
The most promising method for controlling the precursor reactivity may be via the single-source method, which eliminates the need for the highly reactive fluorine sources. Our first attempt towards a single-source precursor was the synthesis of bis-(trifluoromethylcyclopentadienyl) calcium. The reaction between  $\text{CF}_3\text{Cp Ti}$  and  $\text{CaI}_2$  failed to give any isolable calcium containing molecules. Based on previous work on  $\text{CF}_3$  substituted cyclopentadienyl metal derivatives,<sup>7</sup>  $(\text{CF}_3\text{C}_5\text{H}_4)_2\text{Ca}$  is not expected to be stable at room temperature.

Another approach towards single-source precursors is based on nitrogen analogues of the diketonate ligands. Reaction of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HFAC) with ethylenediamine gives the cyclic molecule (1) shown below.<sup>8</sup> Analogous molecules are produced when o-phenylenediamine or m-phenylenediamine are used instead of the ethylenediamine. The syntheses of these last two molecules have not been reported previously. Interestingly, p-phenylenediamine reacted with HFAC to give a different type of product, presumably due to steric reasons. The phenylenediamines were chosen to prevent nitrogen incorporation into the film. Bonds between nitrogen and aryl carbon atoms are very strong, therefore, the phenylenediamine units should stay intact during the deposition reaction, which will prevent nitrogen incorporation.



Each of these ligands react with finely divided calcium metal to produce the calcium complexes. Unfortunately, these complexes were found to be rather nonvolatile, and too unreactive to be good precursors.

Currently, work is proceeding on molecules with similar architectures shown below. This has been hindered by the commercial nonavailability of 1,1,1,2,2-pentafluoro-5-phenyl-3,5-pentanedione. Work is currently in progress aimed at isolation and characterization of the calcium derivatives



### *Conclusions*

CVD of calcium fluoride is severely hampered by the lack of good calcium precursors, for both single-source and dual source approaches. The dual-source technique suffers from a problem of the fluorine source and the calcium source reacting upon mixing, which leads to deposition on the walls of the reactor, and not on the substrate. Currently, there are no good single-source precursors that are not expected to lead to significant oxygen incorporation in the film, or on a bare semiconductor surface. From this work, we feel that we have identified the characteristics needed for good calcium fluoride precursors, and continue to prepare specifically designed single and dual source precursors for calcium fluoride deposition.

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